ELECTRONIC ENERGY STATES IN ONE DIMENSIONAL CRYSTALS

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ABSTRACT. Investigations have been made about the electronic energy state in one dimensional crystals within the frame work of rectangular potential-well model A matrix method, similar to that of Saxon and Hutner, has been used. The key role in determining the energy band structures under different physical conditions is shown to be played essentially by the trace of a matrix which has been named as T-matrix in the text Comparative discussion has been given about the matrix method used here and that used by Luttinger. Both perfect and disordered crystals have been studied and explicit energy band equations have been given for both cases. Results for the disordered case have been given only upto first-order and in a form which is suitable for numerical computation for any type of disorder.

INTRODUCTION

Quantum-mechanical investigation of the physical properties of solids needs solution of Schroedinger equation for one-electron wave functions with appropriate potential field in which the electrons move inside the solid For a perfect infinite crystal, the potential energy of electrons inside the solid is assumed to be a periodic function with periodicity equal to that of the lattice It is well-known that the energy eigen-spectrum of electrons moving in such a periodic potential is divided into allowed and forbidden bands. In reality, one has to solve a three-dimensional problem. However, a lot of insight into the nature of the real three dimensional crystal can be obtained by a study of the one-dimensional case (Fues *et al*, 1952) For a one dimensional solid, the mathematical problem is to find the allowed and regions of the solution of the equation :

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi = 0 \qquad \ldots (1)$$

where E is the total energy and $V(x)$ is the $P.E$ of the electron. For a perfect crystal $V(x)$ is a periodic function with lattice periodicity. For a disordered or amorphous solid $V(x)$ loses this property of periodicity and one faces difficulty in solving equation (1) to an extent depending on the degree of deviation of $V(x)$ from periodicity.

In applying equation (1) to the study of a perfect crystal, extensive use has been made of sinusoidal and Kronig-Penney δ-potentials. As has been discussed by Allen (1953), the band structures for these models do not show all the characteristics of the band structures for real crystals. Thus for both these models, the band-

structures do not show points of contact between different allowed bands while in actual solids these bands exist and they play an important role in the study of surface states, as has been shown by Shockley (1939). The band structure for Krong-Penney potential differs from that of the real crystal in another respect. While in the Krong-Penney case, the size of the forbidden regions approaches a constant nonvanishing value as $E \to \infty$, in the actual case the forbidden ranges of energy approach zero as $E \to \infty$. The band structure for the case of a finite rectangular potential-well, on the other hand, has the proper behaviour as $E \to \infty$ and has an infinite no. of points of contact.

What has been said so far points out the importance of the rectangular potential-well model in investigating the electornic energy-band structures in solids. It has been the aim of this paper to make a thorough investigation of the electronic energy states in one-dimensional monoatomic crystal within the frame-work of the rectangular potential-well model. A matrix method, developed after a work of Saxon and Hutner (1949), has been used. The energy-band structures under different physical conditions are shown to depend essentially upon the trace of a matrix which has been named as 'T-matrix' (details given later). The general features of this T-matrix in connection with energy-band structures have been pointed out. Comparative discussion has been given about the matrix method used here and that of Luttinger (1951) Investigations have been made about perfect and disordered systems Explicit energy-band equations for both these cases have been given. The effect of disorder on the electronic energy-states has been calculated only upto first order. Although not done in this paper, the first order disorder equation for electronic energy-states is in a form which can be put to numerical computations

MODEL AND THEORY

We consider the motion of an electron in monoatomic one dimensional crystal where the potential energy of the electron is assumed to have the form given by Fig. 1.

Each of the potential energy wells may be considered a rough approximation for the potential in the vicinity of an atom. Schroedinger equations for the motion of the electron are given by the following :

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \qquad \ldots \quad (2)$$

for regions like $b < x < a+b$.

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0 \qquad \ldots \quad (3)$$

for regions like $0 < x < b$.

We assume that $E < V$. The general solutions of equations (2) and (3) are given respectively by the following equations :

$$\psi(x) = A \exp(i\alpha x) + B \exp(-i\alpha x) \quad \ldots (4)$$

$$\psi(x) = C \exp(\beta x) + D \exp(-\beta x) \quad \ldots (5)$$

where,

$$\alpha^2 = \frac{2mE}{\hbar^2} \quad \ldots (6)$$

$$\beta^2 = \frac{2m(V-E)}{\hbar^2} \quad \ldots (7)$$

Considering now an x-interval equal to one period say from $x = 0$ to $x = a+b$, we can write :

$$\begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = T \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} \quad \ldots (8)$$

In equation (8), T is a 2×2 matrix and plays a role similar to the scattering matrix of Saxon and Hutner (1949). A_1 and B_1 are the constants for equation (4) at $x = a+b$ while A_0 and B_0 are the corresponding constants at $x = 0$. T can be written as a product of some other matrices in the following form :

$$T = sRvr \quad \ldots (9)$$

s and v are translational matrices given by the following

$$s = \begin{pmatrix} \exp(i\alpha a) & 0 \\ 0 & \exp(-i\alpha a) \end{pmatrix} \quad \ldots (10)$$

$$v = \begin{pmatrix} \exp(\beta b) & 0 \\ 0 & \exp(-\beta b) \end{pmatrix} \quad \ldots (11)$$

R and r are matrices which correlate A and B of eqn (4) to C and D of eqn (5) at points like $x = b$, $a+2b \ldots$ or at points like $x = 0$, $a+b \ldots$etc.

Explicitly,

$$\begin{pmatrix} A \\ B \end{pmatrix}_{\text{at } x=b,\ a+2b \ldots \text{ etc}} = R \begin{pmatrix} C \\ D \end{pmatrix}_{\text{at } x=b,\ a+2b \ldots \text{ etc}} \quad \ldots (12)$$

or at $x=0$, $a+b \ldots$ etc — or at $x=0$, $a+b \ldots$ etc

$$\begin{pmatrix} C \\ D \end{pmatrix}_{\text{at } x=b,\ a+2b \ldots \text{ etc}} = r \begin{pmatrix} A \\ B \end{pmatrix}_{\text{at } x=b,\ a+2b \ldots \text{ etc}} \quad \ldots (13)$$

or at $x=0$, $a+b \ldots$ etc — or at $x=0$, $a+b \ldots$ etc

Using the continuity conditions for the wavefunctions and their derivatives, one gets the following results for R and r

$$R = \frac{1}{2i\alpha}\begin{pmatrix} i\alpha+\beta & i\alpha-\beta \\ i\alpha-\beta & i\alpha+\beta \end{pmatrix} \quad \ldots (14)$$

$$r = \frac{1}{2\beta}\begin{pmatrix} i\alpha+\beta & \beta-i\alpha \\ \beta-i\alpha & i\alpha+\beta \end{pmatrix} \quad \ldots (15)$$

We notice that the matrix $T' = Rvr$ correlates the coefficients A and B of equation (4) at points $x = 0$ and $x = b$ and similar pairs of points at other potential wells through the equation :

$$\begin{pmatrix} A \\ B \end{pmatrix}_{\text{at } x=b,\ a+2b \ldots \text{ etc}} = T' \begin{pmatrix} A \\ B \end{pmatrix}_{\text{at } x=0,\ a+b \ldots \text{ etc}} \quad \ldots (16)$$

When $b \to 0$ so that bV remains finite (δ-potential), we find that .

$$T' = \begin{pmatrix} 1-iP/\alpha & -iP/\alpha \\ iP/\alpha & 1+iP/\alpha \end{pmatrix} \quad \ldots (17)$$

where,

$$P = \frac{mbV}{\hbar^2} \quad \ldots (18)$$

The matrix (17) is just the 'R' matrix for δ-potential as obtained by Saxon and Hunter (1949)

Now a straight forward calculation gives the following expressions for the elements of the T-matrix :

$$T_{11} = \frac{1}{4i\alpha\beta}[(i\alpha+\beta)^2 \exp(\beta b+i\alpha a)-(i\alpha-\beta)^2 \exp(-\beta b+i\alpha a)] \quad \ldots (19)$$

$$T_{22} = T_{11}^* \quad \ldots (20)$$

$$T_{21} = \frac{1}{4i\alpha\beta}[(i\alpha+\beta)(i\alpha-\beta) \exp(-i\alpha a)\{\exp(\beta b)-\exp(-\beta b)\}] \quad \ldots (21)$$

$$T_{12} = T_{21}^* \quad \ldots (22)$$

By a straight forward calculation it is also found that $det\ T = 1$. The T-matrix here is the same as the H-matrix derived by a different method by Kerner (1954).

General features of T-matrix.

(1) Condition for allowed and forbidden bands: We consider a ring of n

atoms. By repeated application of equation (8) from one cell to another, we can write:

$$\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = T^n \begin{pmatrix} A_1 \\ B_1 \end{pmatrix} \tag{23}$$

But $(n+1)$ the cell is the same as the first cell. This means

$$T^n \begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = \begin{pmatrix} A_1 \\ B_1 \end{pmatrix} \quad \ldots \quad (24)$$

Eqn (24) is similar to the one derived by Luttinger (1951). We shall later on present discussions about Luttinger's equation compared to (24) Here we follow his argument to find the connection of the T-matrix with the energy-band structure We notice from (24) that the allowed energies correspond to the eigenvalue 1 of the matrix T . This again shows that the allowed energies correspond to the n-th roots of unity for the matrix T. Thus the allowed energy levels are obtained by setting the eigenvalues of T equal to $\exp(\pm 2ik\pi/n)$ where k is an integer satisfying $0 \leqslant k \leqslant (n-1)$. When n is very large, the different values of k gives us for $k\pi/n$ practically the continuum from zero to π. This is what we mean by an allowed band in a finite crystal The allowed band is thus determined by those values of the energy which make the eigenvalues of T complex numbers whose absolute value is unity. Since $det\ T = 1$, the secular equation for the eigenvalues of T is given by.

$$\lambda^2 - (T_r T)\lambda + 1 = 0$$

or

$$\lambda \pm = \frac{T_r \pm \sqrt{(T_r T)^2 - 4}}{2} \quad \ldots \quad (25)$$

Now if $T_r T \leqslant 2$, $\lambda_+ = \lambda_-^*$ and $|\lambda_+|^2 = |\lambda_-|^2 = 1$,

so that we have allowed energies If $\mathrm{Tr}\ T > 2$, both the eigenvalues are real. One of them is of absolute value greater than unity and the other of absolute value less than unity. This means that the condition for the forbidden level is simply $|\mathrm{Tr}\ T| > 2$ ... (26)

(2) Properties of $\mathrm{Tr}\ T$ in relation to energy bands · we note that T-matrix is not Hermitian. Had it been so, the eigenvalues would always have been real. which means $\mathrm{Tr}\ T > 2$. All energies would thus have been forbidden. Again if $\mathrm{Tr}\ T \leqslant 2$ always, the eigenvalues are always complex satisfying $|\lambda_+|^2 = |\lambda_-|^2 = 1$. In this case all the energies would have been allowed In either case one does not get a band structure. Thus the occurrence of allowed and forbidden bands of electronic energies in a crystal is equivalent mathematically to saying that T is neither Hermitian nor $\mathrm{Tr}\ T \leqslant 2$ always. We now examine the circumstances under which T-matrix assumes these extreme forms.

Case I · Suppose V = constant and $E > V$. We can easily see that in this case $\beta = i\alpha$, $\alpha^2 = \frac{2m}{\hbar^2}(E-V)$. From (19) and (20) it then follows that Tr $T = 2\cos\alpha(a+b)$ ... (27)

$$T = \begin{pmatrix} T_{11} & 0 \\ 0 & T_{11}^* \end{pmatrix} \quad \ldots (28)$$

$$\lambda\pm = \cos\alpha(a+b) \pm i\sin\alpha(a+b) \quad (29)$$

Thus in this case T is not Hermitian, Tr $T \leqslant 2$ and $|\lambda_+|^2 = |\lambda_-|^2 = 1$, for all values of α. This means that $(E-V) = E_k$, the K.E. of the electron can take all values (no band structure) from 0 to ∞ This is the well known result for the electronic energy spectrum in the free-electron model.

Case II . Suppose V = const and $E < V$. Then in this case

$$\beta = i\alpha \quad \beta^2 = \frac{2m}{\hbar^2}(V-E), \quad \text{Tr } T = 2\cosh\beta(a+b) \quad \ldots (30)$$

$$\lambda\pm = \cosh\beta(a+b) \pm \sinh\beta(a+b) \quad \ldots (31)$$

$$T = \begin{pmatrix} \exp\beta(a+b) & 0 \\ 0 & \exp\{-\beta(a+b)\} \end{pmatrix} \quad \ldots (32)$$

Thus in this case Tr $T > 2$ always, $|\lambda_+|^2 \neq 1$, $|\lambda_-|^2 \neq 1$ and T is Hermitian Hence all the energies below V are forbidden This means that there are no electrons inside the crystal with total energy less than the potential energy which is constant throughout the lattice. This conclusion is again consistent with the actual physical situation.

EXPLICIT ENERGY EIGENVALUE EQUATIONS

We now use the T-matrix to derive energy eigenvalues for some special cases.
Case I Perfect infinite crystal · Considering the model of Fig. (1) and noting that

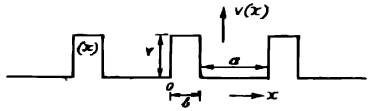

Fig. 1

Rectangular potential-well model for a one-dimensional monoatomic perfect crystal.

for such an infinite crystal, Bloch's theorem must hold good, we can write :

$$\begin{pmatrix} A_1 \\ B_1 \end{pmatrix} = \exp i\mu(a+b) \begin{pmatrix} A_0 \\ B_0 \end{pmatrix} \quad \ldots (33)$$

From (8) and (33), (using det $T = 1$), one gets :

$$\cos\mu(a+b) = \tfrac{1}{2}\,\text{Tr}\,T \quad \ldots (34)$$

Eqn (34) shows that $|\operatorname{Tr} T| \leqslant 2$, which is the same as derived earlier by applying periodic boundary condition to a circular chain. Using T_{11} and T_{22} from (19) and (20), we get from (34),

$$\frac{\beta^2-\alpha^2}{2\alpha\beta} \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos \mu(a+b) \tag{35}$$

Eqn. (35) is the same as that derived by other workers

Case II. One dimensional monoatomic disordered solid Let us consiger the model of the solid as given by Fig. (2) below

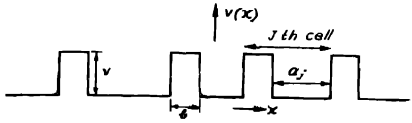

Fig. 2

Rectangular potential well model for a one dimensional monoatomic disordered solid.

Distances such as a_j for the j-th cell are arbitrary They are represented by :

$$a_j = a + \epsilon_j \qquad \ldots (36)$$

where a is the average of all a_j's and ϵ_j's are fluctuations over a From eqn (9) we find that the T-matrix for the j-th cell is given by

$$T_j = \begin{pmatrix} \exp i\alpha(a+\epsilon_j) & 0 \\ 0 & \exp\{-i\alpha(a+\epsilon_j)\} \end{pmatrix} \qquad \ldots (37)$$

We note from (37) that $\det T_j = 1$ for all j's Suppose there are n-cells in the lattice. By applying periodic boundary condition and following the same argument as used in getting eqn (24) for a perfect lattice, we get the following equation for present case :

$$\begin{pmatrix} j=1 \\ \pi T_j \\ j=n \end{pmatrix} \begin{pmatrix} A_1 \\ \\ B_1 \end{pmatrix} = \begin{pmatrix} A_1 \\ \\ B_1 \end{pmatrix} \qquad \ldots (38)$$

Thus the eigenvalues of (πT_j) are equal to 1. For the present model, the crystal of n-cells is one period Hence the matrix (πT_j) for the present model plays the same role as the matrix T for Fig. (1). Thus the eigen-values of (πT_j), like those of T, are complex numbers with absolute value unity—conforming to eq (38). Since $\det T_j = 1$ for all j, $\det(\pi T_j) = 1$ and the secular equation for the eigenvalues of (πT_j) is given by :

$$\lambda_{\pm} = \frac{\operatorname{Tr}(\pi T_j) \pm \sqrt{(\operatorname{Tr} \pi T_j)^2 - 4}}{2} \qquad \ldots (39)$$

Thus in the present case, the allowed energies are given by the condition

$$\mathrm{Tr}\,(\pi T_j) \leqslant 2 \qquad \ldots \quad (40)$$

From (37), retaining only the first order term,

$$T_j = (T + K_j T) \qquad \ldots \quad (41)$$

where,

$$K_j = \begin{pmatrix} i\alpha\epsilon_j & 0 \\ 0 & -i\alpha\epsilon_j \end{pmatrix} \qquad \ldots \quad (42)$$

With the help of (42), we get by retaining again only the first order terms

$$(\pi T_j) = T^n + \sum_{\gamma=1}^{\gamma=n} T^{n-\gamma} K_j T^{\gamma} \qquad \ldots \quad (43)$$

From (40) and (43) equating zero and first order terms separately to zero, we get

$$T_r T^n \leqslant 2 \qquad \ldots \quad (44)$$

$$T_r \left(\sum_{\gamma=1}^{\gamma=n} T^{n-\gamma} K_j T^{\gamma} = 0 \right) \qquad \ldots \quad (45)$$

Eqn (44) shows that the energy eigen values for the model considered here retain the band structure characteristic of a perfect crystal with periodicity na. Eqn (45) gives the extra energy-values due to disorder. We now proceed to find explicit forms of equations (44) and (45).

The similarity transformation for diagonalisation of T matrix is given by

$$XTX^{-1} = \begin{pmatrix} \exp(ic) & 0 \\ 0 & \exp(-ic) \end{pmatrix} \qquad \ldots \quad (46)$$

$$X = \begin{pmatrix} T_{21} & \exp(ic) - T_{11} \\ T_{21} & \exp(-ic) - T_{11} \end{pmatrix} \qquad \ldots \quad (47)$$

$$X^{-1} = \frac{1}{\det X} \begin{pmatrix} \exp(-ic) - T_{11} & T_{11} - \exp(ic) \\ -T_{21} & T_{21} \end{pmatrix} \qquad \ldots \quad (48)$$

$$\cos c = \tfrac{1}{2}\,\mathrm{Tr}\,T \qquad \ldots \quad (49)$$

Eqn (49) satisfies the requirement that $\mathrm{Tr}\,T \leqslant 2$ and gives $\exp(ic)$ and $\exp(-ic)$ as the eigenvalues of T. Hence the diagonal form (46). From (46), (47) and (48), we can easily show the following :

$$(T^n)_{22}{}^* = (T^n)_{11} = \frac{1}{\sin c} \{\sin(n+1)c - T_{11}{}^* \sin nc\} \qquad \ldots \quad (50)$$

$$(T^n)_{21} = (T^n)_{12}{}^* = T_{21}\frac{\sin(nc)}{\sin c} \qquad \ldots \quad (51)$$

Thus with the help of (50), eqn (44) takes the form :

$$\frac{1}{\sin c}\{\sin(n+1)c - T_{11r}\sin(nc)\} \leqslant 1 \qquad \ldots \quad (52)$$

where,

$$T_{11}{}^* = T_{11r} + i\,T_{11} \qquad \ldots \quad (53)$$

Using eqns (46), (47) and (48) and retaining only the first order terms, eqn (45) can be simplified to the following form :

$$\sum_{j=1}^{j=n} \epsilon_j[T_{11I}\cos(n-2j-1)c - 2T_{11r}T_{11I}\}\cdot$$

$$\cdot\cos(n-2j)c + T_{11I}\cos(n-2j+1)c] - 2\left(\sum_{j=1}^{j=n}\epsilon_j\right)T_{11I}\varsigma\,.$$

$$\cdot\cos(n+1)c - T'_{11}\cos nc] = 0 \qquad \ldots \quad (54)$$

where,

$$T_{12} = T_{12r} + iT_{12I} \qquad \ldots \quad (55)$$

If the fluctuations ϵ_j's are all random, the different terms in the summation $(\Sigma\epsilon_j)$ may cancell one another and the net effect of the second terms in (54) will be practically zero. The extra energy levels due to disorder of system will thus be predominantly determined by the first term of (53) when the fluctuations ϵ_j's are all random.

DISCUSSIONS

In the work of this paper, we have demonstrated the use of T-matrix in getting energy-band equations for one dimensional crystals. The critical role in determining the band structure is shown to be governed by Tr T We have shown that for allowed energies Tr $T \leqslant 2$. Luttinger (1951) has derived a similar condition but his result is expressed through an 'A' matrix. The elements of A-matrix are again expressed through y-solutions of James (1949). Luttinger has discussed some characteristics of energy bands in pure and mixed lattices and for this purpose it is enough to know only some general properties of the A-matrix (like det$A=1$, $A_{11}=A_{22}$) However, for knowing explicitly the energy-eigenvalue equations, one must know exactly the matrix which correlates the co-efficients of thecell-to-cell wave functions. This purpose has been served by the T-matrix since for the type of potential considered, we have been able to knowthe exact form of the elements of T-matrix.

We note here that in deriving eqn (54) for the energy values due to disorder, no assumption other than that of neglecting second and higher order terms—has

been made Thus equation (54) can be put to numerical computations for any type of fluctuations c_p. It can also be seen that the method illustrated here can be used to study the energy band structures of mixed lattices. This problem is under author's contemplation and the results will appear in later publications.

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